PAT monitoring and PBE modelling of batch cooling solution crystallization in the presence of impurities

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PAT MONITORING AND PBE MODELLING OF BATCH COOLING SOLUTION CRYSTALLIZATION IN THE PRESENCE OF IMPURITIES.

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Hindering effects of impurities on the crystal growth are usually assumed to result of the adsorption of impurity species on the crystal surface. In the presence of impurities the growth rate does not depend on supersaturation only, but also on the concentration of impurities and on the time a given particle spent in contact with inhibiting species (unsteady-state adsorption mechanisms). Few kinetic models describe such phenomena. Moreover, published models are derived from data obtained from specific experiments performed on singles crystals, which makes their application to real industrial crystallizers rather questionable. Indeed, for process engineering purposes, the available kinetic inhibition models accounting for the effect of impurities (e.g. Cabrera-Vermilyea[1] or Kubota-Mullin's[2] approaches), have to be evaluated in industrial situations where complex and distributed features of the crystallizing suspensions are involved (e.g. during batch solution crystallization). Population Balance Equations (PBE) modelling offer an invaluable simulation tool for such evaluation.
With this aim in view, a comprehensive modelling approach based on *in situ* continuous and dispersed phase measurements, and specific PBE simulation was developed to represent and better understand the effect of impurities on the development of batch crystallization processes.
The cooling solution crystallization of Ammonium Oxalate (AO) in water in the presence of various concentration of Nickel Sulphate was selected as a model system during this study. In situ measurements of supersaturation were performed using ATR-FTIR spectroscopy and the CSD was assessed thanks to *in situ* image acquisition followed by off-line image processing. The experimental results were simulated after estimating crystallization kinetic parameters, including parameters of models describing the inhibiting adsorption of impurity on the growing crystal surfaces. Nonlinear optimization techniques were used to fit the experimental data to the simulated ones.
A 3 L temperature-controlled glass vessel was used for the experiments. High efficiency propeller was used to maintain the slurry in suspension. The whole operating device was instrumented to monitor the development of crystallization during linear cooling rate experiments. *In situ* solute concentration measurements were performed using a Brucker FTIR spectrometer equipped with an ATR-diamond immersion probe[3]. In addition to the measurement of supersaturation, the generation of dispersed solid phase was monitored using *in situ* image acquisition performed by an imaging probe developed at the University of Lyon: the "EZProbe"[4]. The recorded images were processed using image analysis and "manual" operations.

AO undersaturated solutions were heated several °C higher than the saturation temperature (50°C). When the ATR-FTIR spectrometer and the EZ-probe indicated complete dissolution, linear unseeded cooling experiments were carried out at different linear cooling rates, namely: 5, 7, 10, 12, 20, 25 and 30°C/h. For each cooling rate, a set of at least 3 experiments was carried out to verify the repeatability of the process. All experiments were stopped at 20°C and left for isothermal stabilization during 3 hours.

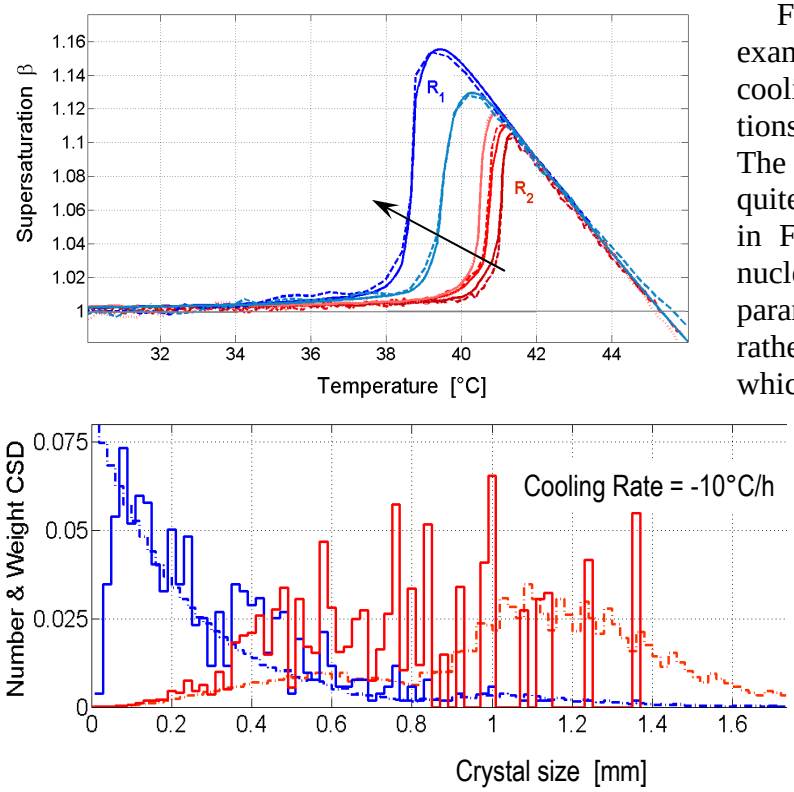

Figure 1 presents typical examples of unseeded batch cooling crystallization operations performed with pure AO. The experimental results were quite reproducible. As displayed in Fig.1, the estimation of the nucleation and growth kinetic parameters allowed designing a rather satisfactory PBE model which led to the conclusion that, according to the cooling rate, two distinct nucleation and growth regimes were occurring (the simulations R_1 and R_2 involve 2 different sets of parameters and refer to as slow and fast cooling, respectively [5])

Figure 1a. Simulated and measured supersaturation profiles during 5 batch cooling crystallization experiments performed with increasing cooling rate (see arrow -5,-7,-10,-25,-30°C/h). b. Number and weight final CSD obtained with dT/dt=-10°C/h.

PBE Modeling. When small amounts of Nickel Sulfate are dissolved in the initial mother liquor, the measured supersaturation profiles are significantly modified, as displayed in Fig 2. Roughly speaking, the onset of primary nucleation is delayed, the growth rate is reduced and the solute concentration profile is clearly unusual. The high level of supersaturation reached at the onset of nucleation does not help the subsequent supersaturation to increase until a second late nucleation burst. It turned out that reproducing such atypical features of the supersaturation profile cannot be achieved without assuming significant and complex inhibition of the crystal growth rate by impurities. Several models can be used for that purpose and Kubota-Mullin's Unsteady-State Adsorption (KMUSA)[6] model gave satisfactory results, except during the final isothermal batch period where the inhibition of solute consumption was really overestimated by the model.

Indeed, when KMUSA model predicts a constant residual level of supersaturation, the measurements demonstrate that the solute concentration returns slowly to solubility. To reproduce these experimental dynamic features of the process and the time variation of

the CSD, the inhibition model thus required to be refined. First, it was assumed that not only Ni^{2+} ions were adsorbed at the crystal surface, but also SO_4^{2-}. Second, *in situ* video monitoring of the crystallization showed a significant increase of the particle number during the process in impure solvent: as time goes on, the particles seem to embrittle and to lose their transparency: this is clearly shown in Fig.2.

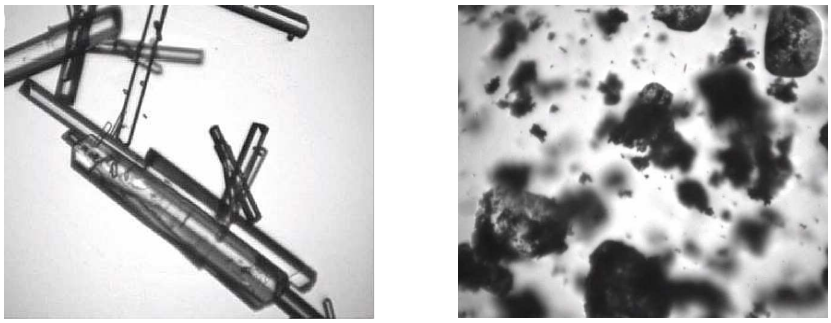

Figure 2. Picture of AO crystals grown in pure water (left) and in the presence of NiSO4 (right)

The following PBE model was applied to simulate the batch crystallization process[7]:

$$\begin{cases} \dfrac{\partial \phi(L,t,\nu)}{\partial t} + G(t,\nu)\dfrac{\partial \phi(L,t,\nu)}{\partial L} = 0 & (1) \\ \phi(L,0,\nu) = 0 & \\ \phi(0,t,\nu) = \dfrac{R_N(t)}{G(t,\nu)}\delta(t-\nu) & (2) \end{cases}$$

$$G(t) = G_0(t)\left(1 - \alpha\theta^* \left[1 - exp\left(-\frac{(t-\nu)}{\tau}\right)\right]\right) \quad (3)$$

"Standard" PBEqs (1-3) were set in order to account for the "birth-date" ν of the particles [7]. $G_0(t)$ refers to the growth rate in pure solvent and G(t) is the inhibited growth rate assuming unsteady-state pinning effect of adsorbed impurities. θ^* is the equilibrium coverage of growing surfaces by adsorbed impurities and τ is the adsorption time constant [4]. As two adsorbed species are involved, θ^* was finally expressed as:

$$\theta^* = \theta^*_{SO_4{}^{2-}} + \theta^*_{Ni^{2+}} = \theta_1^* + \theta_2^* \; with \quad \theta_i^* = \frac{K_i C_i}{1 + K_i C_i + K_j C_j} \; and \; K_i = \exp\left[\frac{-E_{ads,i}}{RT}\right] \quad (4)$$

Several nucleation and growth models were evaluated for their ability to account for the observed experimental variables. The following expressions were selected to represent the process dynamics [8]:

$$G_0(\sigma) = k_g \; \sigma^2 \; and \quad R_{N_1}(\beta) = \mathrm{A}\exp\left[\frac{-\mathrm{B}}{\mathrm{T}^3(\ln\beta^2)}\right] \quad and \; R_{N_2}(\sigma) = D\; {C_s}^j \; \sigma \quad (5\text{-}7)$$

Some kinetic parameters involved by Eqs.(5-6) were taken from previous parameter estimations performed using the experimental results in pure water. Other parameters describing the inhibiting effects of $NiSO_4$ were estimated after fitting the PBE simulated variable to the experimental data which are partly shown in Fig. 3. Exponent j was found between 8 and 10 which is unrealistic if one consider contact phenomena between particles but, consistently with Fig.2b, might be regarded as a way of accounting for multiple breakage phenomena observed in impure media.

In addition to the important problem of estimating unreasonable number of parameters, setting the involved values of adsorption energy (see Eq.4)) raised some difficulties.

The latter were therefore computed separately through molecular simulation of the adsorption of Ni^{2+} and SO_4^{2-} on AO crystal surfaces. The computed values were introduced in the model without further correction.

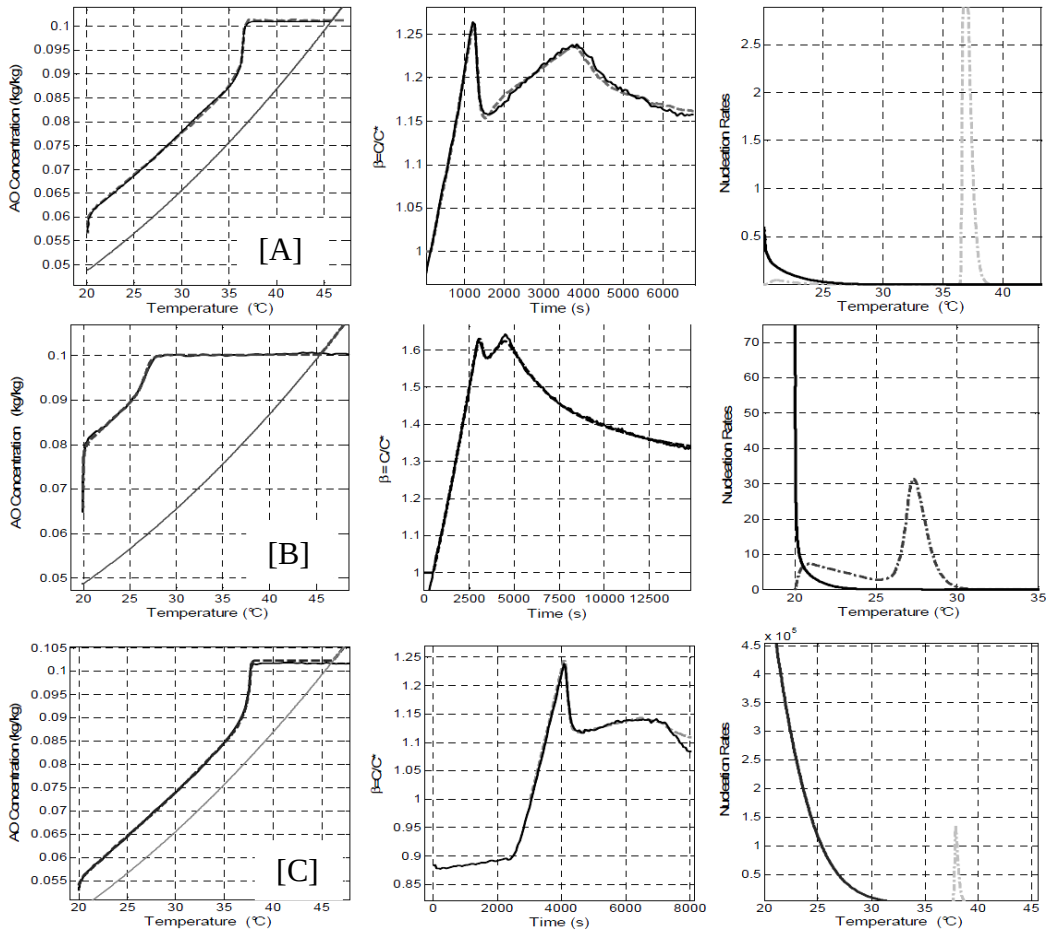

Figure 3. Experim. data (solid lines) and simulation (dashed lines) of crystallization operations performed at the same cooling rate (-30°C/h) and simulated primary (dashed-dot lines) and secondary nucleation rates (solid lines). Impurity concentrations: A) 1%; B) 5.4% C) 0.5 %.

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